Isotopically Controlled Silicon Single Crystals

Multinational Teams Determine Bandgap in Ultrapure Crystals

Eugene Haller and Joel Ager of MSD's Electronic Materials Program have synthesized ultrapure single crystals of silicon, each enriched in one of its three stable isotopes: ^{28}Si, ^{29}Si, and ^{30}Si. As a first example of the value of these unique materials, they were used to make the most precise measurement to date of silicon's band gap, which is the most fundamental property of any semiconductor

Close to 80% of the elements in the periodic table are multi-isotopic; thus most multi-element semiconductors contain at least one element that consists of more than one stable isotope. For example, silicon is composed of the three stable isotopes ^{28}Si, ^{29}Si, and ^{30}Si with natural abundances of 92.23%, 4.67% and 3.10%, respectively. While many physical properties of semiconductors are not significantly affected by isotopic composition, others—thermal conductivity for example—can be influenced strongly. In a material with a larger average atomic mass M (e.g. enriched ^{30}Si), the average atomic displacement (the distance over which the atoms move as the crystal vibrates) is smaller. This has two well-known effects: both the lattice constant (average distance between atoms) and the coupling between the electrons and the phonons (vibrations in the crystals) decrease. It is further known that decreasing the lattice constant and the electron-phonon coupling increase the bandgap. As a result, increasing M is predicted to increase the band gap of a semiconductor by a small, but observable amount.

A careful study of the Ge bandgap was performed in the mid-1990's using ultrapure isotopically controlled crystals grown at LBNL. Surprisingly, given its importance in science and technology, similar measurements had not been performed in Si. The reason for this lies in part in the high cost of isotopic enrichment and in part in the stringent chemical purity requirements—most impurities need to be below the ppm level, and some well below the ppb level in order for precision measurements to be made. Although the first isotopically enriched Si was made in the late 1950's, crystals with both high isotopic enrichment and the requisite chemical purity had not been produced.

The LBNL researchers addressed this challenge by designing and implementing a laboratory-scale process specifically designed to attain high chemical purity and high yield. The latter requirement is essential due to the limited amounts of isotopically enriched precursors that are practically available. The enrichment step was performed (with funding from the DOE Initiatives for Proliferation Prevention Program) to LBNL's specifications by the Electrochemical Plant in Zelenogorsk, Russia with gaseous SiF_4 using centrifuge technology originally developed for high-volume uranium processing. SiF_4 was converted to silane (SiH_4) by an experienced domestic vendor. The silane was decomposed to form a high purity polycrystalline silicon rod in a reactor designed and built at LBNL. Finally, three single crystals of silicon (99.92% ^{28}Si, >90% ^{29}Si, >90% ^{30}Si) were "pulled" from the poly-Si rods using the floating zone process at the Institut für Kristallzüchtung, Berlin. These crystals are among the highest quality isotopically enriched Si made to date with electrically active impurities at 10^{15} cm^{-3} and below, low carbon concentrations, and minimal amounts of inhomogeneous lattice strain.

As shown in the figure, precise optical measurements of the bandgap were made by collaborators at Purdue University. By performing these measurements on crystals with different average masses, it was established that the value of the purely electronic Si bandgap, in the absence of all electron-phonon interaction and volume change effects, is 1.2138 eV.

Research is continuing, both in exploring fundamental properties of these unique materials and developing methods to make crystals with even higher enrichments and chemical purity. ^{28}Si-enriched material has been proposed as a "nuclear-spin-free" matrix for solid state quantum computing designs. In this context, a recent magnetic resonance study of LBNL's ^{28}Si-enriched crystal found that the key figure of merit for quantum computing schemes, namely, the electron spin decoherence time (T_2) of electrons bound to phosphorus, which is present as an impurity in the crystal at 10 ppb, is the longest ever measured in Si (5 ms, more than a factor of two longer than the previous record and long enough to meet the requirement for quantum error correction).

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Basic research in the Electronic Materials Program is supported by the Division of Material Science, BES, Office of Science, DOE. Isotopically enriched precursors were purchased with funding from the DOE Initiatives for Proliferation Prevention Program of the Office of Nonproliferation Research and Engineering (NN-20). Purdue University researchers were supported by NSF.

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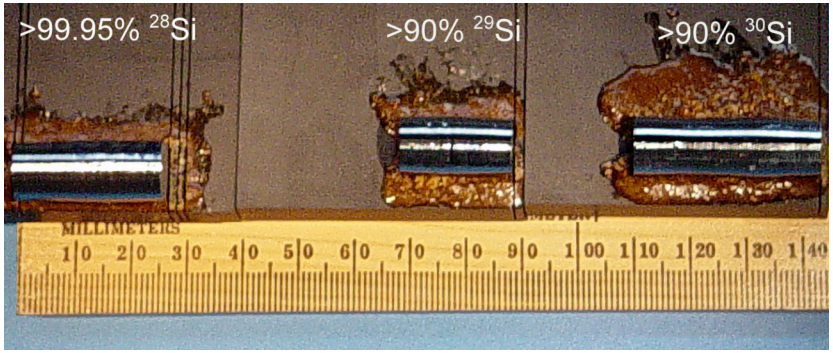
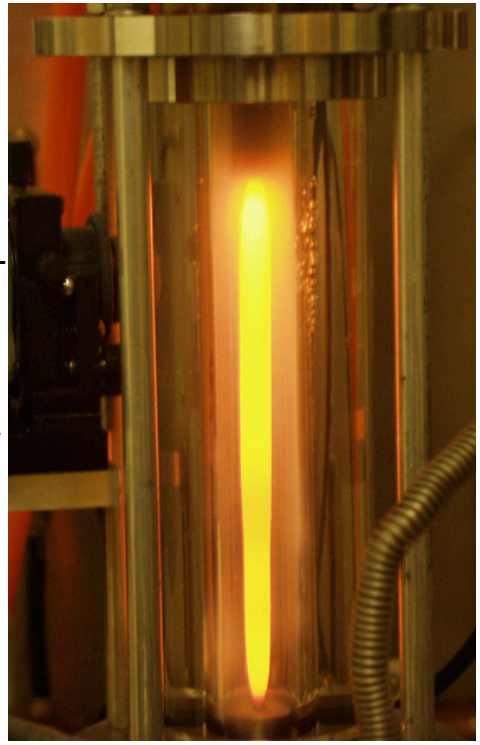
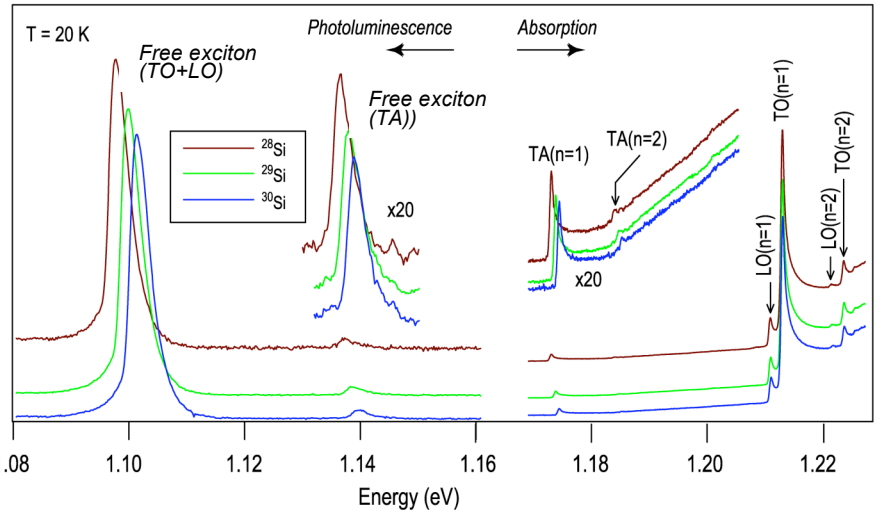
Multinational Teams Determine Band Gap in Unique, Ultrapure Crystals

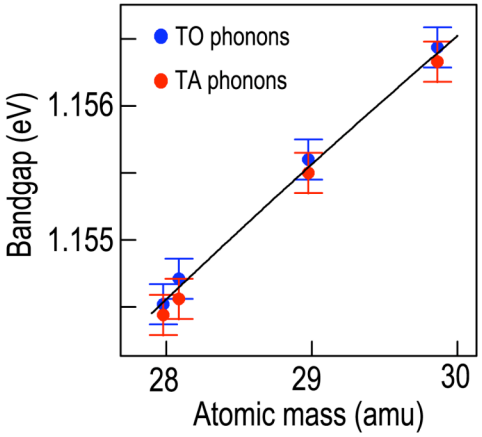


Dislocation-free, single crystals *enriched in each one of the three stable isotopes of Si grown from high purity LBNL poly-Si (above). Deposition of poly-Si at 730°C from ^{28}Si-enriched silane in a high-purity, high yield LBNL reactor (right).*



Optical absorption *and photoluminescence (PL) across the indirect gap of silicon occur with assistance from phonons (TA, LO, and TO where T = transverse, L = longitudinal, O = optical, and A = acoustic). Absorption peaks are observed at the band gap plus the phonon energy; PL peaks are at the band gap minus the phonon energy.*





By matching transitions *assisted by the same phonons the precise value of the band gap as a function of mass is obtained by interpolation. The purely electronic Si bandgap, in the absence of all electron-phonon interaction and volume change effects, is 1.2138 eV.*

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